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Production of enriched methane by a molten-salt concentrated solar power plant coupled with a steam reforming process: An LCA study

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ABSTRACT

Enriched Methane is a gas mixture consisting of methane and a certain amount of hydrogen (10–30%vol) that finds out several applications such as fuel of Internal Combustion Engines (ICEs). To produce EM, a steam reforming reactor whose heat duty is supplied by a molten-salt stream heated up by a concentrating solar power (CSP) plant can be used, in order to generate the hydrogen steam by solar energy. In fact, molten salts at temperatures up to 550 °C can allow to reach the necessary thermal level inside the reactor to promote steam reforming reaction.

The combination of technologies such as EM steam reformer, concentrating solar power (CSP) systems and molten-salt heat carriers, allows a partial decarbonation of the fossil fuel, thanks to the production of hydrogen, together with the possibility to carry solar energy in the current natural gas grid.

The aim of this work is to present a Life Cycle Assessment of a novel hybrid plant for the production of EM from a solar steam reforming reactor. The performance, of this innovative architecture have been evaluated from an environmental point of view by the use of a LCA software (SimaPro7) and compared with the ones of traditional plants (reformer and cracker for the hydrogen production). The results highlight the lower environmental footprint of this innovative plant compared to the environmental impact of the two traditional plant considered in this work. The fossil energy duty of the MS-CSP-SR plant is about 50% less than that required from the conventional cracker and reformer production plants. The conventional plants are also characterized by a Global Warming Potential of about 75% higher than that of the MS-CSP-SR plant.

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1. Introduction

Enriched Methane (EM) is a gas mixture consisting of methane and a certain amount of hydrogen (10–30%vol). Some literature works [1–4] testify the use of EM in the current methane engines for traction and automotive by providing the following advantages with respect to the sole methane:

- Flames rate increasing;
- Stable combustion even with very lean mixtures;
- Reduced cyclic variability of the engine by allowing an improved accuracy in supplying the fuel [3].

These variations lead to an increase in the engine efficiency, with a consequent reduction of CO_2, CO, and unburned compounds in the order of 20–50% according to the hydrogen concentration in the mixture.

EM application as energy source can be seen as a transitional technology towards a zero-emission energy system on the long-term, where the zero-emission energy system consists of the use of the pure hydrogen. In any case, a mixture of methane and hydrogen with a hydrogen concentration smaller than 30% already takes to concrete advantages in the current energy scenario:

- All the issues related to the hydrogen storage are overcome since the existing storage systems for the methane can be already used to store EM.
- Medium- and low-pressure infrastructures used for the natural gas can be also used for the branched distribution of EM, without the need of any *ad hoc* investment. Actually, as described by the literature [5], no significant technical changes to the secondary gas network are necessary to distribute EM with a percentage of H_2 smaller than the 17% (EM-17).

Hydrogen in mixture with methane can be produced by steam reforming of natural gas, which is the most widespread and well-established technology to generate hydrogen [6]. It is based on the following simplified reaction scheme:

$$CH_4 + H_2O = CO + 3H_2 (\text{steam reforming reaction}) \quad \Delta H^0_{298} = 206\ \text{kJ/mol} \tag{1}$$

$$CO + H_2O = CO_2 + H_2 (\text{water gas shift reaction}) \quad \Delta H^0_{298} = -41\ \text{kJ/mol} \tag{2}$$

The process is endothermic and the reactions take place fast on a Nickel-based catalyst by leading to the thermodynamic equilibrium condition of methane conversion; on this subject, a reasonably satisfactory conversion to hydrogen of the inlet stream is obtained at high operating temperatures (850–1000 °C). The industrial best practice exploits fixed-bed tubular reactors 10–12 m long placed within fired heaters to ensure the required operating temperatures. Natural gas is the reactant of the process and the fuel of burners of the fired heater as well.

The process efficiency in terms of specific heat of the produced hydrogen versus the inlet flow-rate of methane (both the reactant and the fuel) is equal to 60–80% according to the plant size [7]. CO_2 specific emissions are in the range of 8.3–10.1 kg_{CO_2}/kg_{H_2} according to the overall process efficiency.

If the reaction specifics is the production of an EM stream, with a content of hydrogen within the range 10–30%vol, the methane conversion required is much lower than the tradition process one. Therefore, no such high operating temperatures are needed and steam reforming heat duty can be supplied by alternative methods.

In a previous work [8], the potentialities, from an environmental point of view, of the molten-salt concentrating solar power plant have been assessed by the LCA methodology and compared with conventional oil and gas power plants. Shortly, the CSP basically consists of a solar collector field, a receiver, a heat transfer fluid loop and a suitable heat storage system to maximize the “capacity factor” (i.e. productivity) of the solar plant and to provide solar heat at the desired rate regardless of the instantaneous solar radiation availability and fluctuations [9,10]. The heat transfer fluid is an alloy of sodium and potassium nitrates and it is stable up to 550 °C (the value of 550 °C is a safety threshold), which is a temperature suitable for the need of a low-temperature steam reforming.

In this work, the coupling between the steam reforming reactor for production of EM and a molten-salt stream based Concentrating Solar Power (CSP) plant is studied and assessed.

A plant composed by molten-salt CSP and a steam reforming reactor (hereinafter MS-CSP-SR) would allow the production of a EM stream without burning methane and, consequently, reducing the specific CO_2 emission up to 5.5 kg_{CO_2}/kg_{H_2}.

The MS-CSP-MR process technology has already been presented in a previous work [6], here, the aim of this work is to evaluate the performance of the proposed innovative plant, from an environmental point of view, by the use of a Life Cycle Assessment Methodology. The obtained LCA results will be compared with these of conventional plants (reformer and cracker for the hydrogen production) for the production of enriched methane.

2. Functional unit, system boundary and plant systems description

A detailed description of the most important LCA steps is reported in a previous work [8].

In this study three different production plants are compared: MS-CSP-SR production plant, conventional reformer and cracker production plants. Since the MS-CSP-SR production plant analysed in this work is a cogenerative plant able to produce 780 Nm^3/h of enriched methane (17% of H_2) and 3246 MWhe/year of energy, in order to compare the results obtained from the relative LCA studies, we define the functional unit as the production of 1.0 Nm^3 of enriched methane (17% of H_2), while the corresponding electrical energy produced (0.58 kWhe) is assumed as co-product. Therefore, even if there are a multiple production (electricity and enriched methane) no allocation

procedures have been used. Really, as suggested by ISO 14044 [11], the system expansion method has been applied. Following this approach, the electrical energy produced displaces the grid electricity used for the enriched methane production.

The system boundary is defined as cradle to gate, excluding the use phase.

Based on the functional unit and system boundary, we describe the production plant systems as follows.

2.1. *MS-CSP-SR production plant*

The MS-CSP plant has deeply analysed and described in a previous work [8], here we only report a short description.

The solar part of a CSP plant consists of:

- A solar collector field composed by parabolic mirrors;
- A receiver;
- A heat transfer fluid loop;
- A heat storage system.

The mirrors of the solar field concentrate the direct solar radiation on the solar receiver set in the focal line. The heat transfer fluid (molten salt) removes the high temperature solar heat from the receiver and is afterwards collected into an insulated heat storage tank to be pumped on demand to the heat users (steam generators for electricity production through a steam turbine) where it releases its sensible heat. Finally the heat carrier fluid is stored into a lower temperature tank at about 290 °C, ready to restart the solar heat collection loop.

As for the SR chemical plant (hydrogen productivity: 780 Nm^3/h), natural gas stream, after a desulphuration step, is fed to a low-temperature steam reforming reactor, where reactions (1) and (2) are carried out heated by a molten-salt stream outcome from CSP (550 °C).

The outlet gas mixture, composed by unreacted methane and steam, hydrogen, CO and CO_2 is fed to a water–gas shift (WGS) unit, where reaction (2) is supported and hydrogen is produced from CO. Then steam is separated by condensation, the last traces of CO are converted in a Preferential Oxidation (PROX) reactor and CO_2 is removed in a MDEA unit. At the end, a stream of CH_4 and H_2 is produced and the composition is regulated by a pure methane stream addition (see Fig. 1). Molten salt supplies heat duty to the reactor, reducing its temperature. The residual heating fluid sensible heat can be used to generate steam to be fed to a steam turbine for clean electricity production. By this way, the plant is cogenerative since it can be produced both hydrogen in a methane stream (EM) and electricity by using solar energy.

2.2. *Conventional cracker production plant*

The cracker production plant considered in this study is a conventional cracker plant (naphtha used as feedstock) for the production of hydrogen. The production of enriched methane has been obtained adding the needed amount of methane to the hydrogen stream coming from the plant. A part of feedstock is used to produce electricity in a power station (installed power 500 MWe); in particular for 1 Nm^3 of enriched methane (17% of H_2) produced it has been considered a production of 0.58 kWhe. The technology installed refers to year 1988 (year of plant building) and has been considered as an average of 17 different cracker production plants installed in Europe.

2.3. *Conventional reformer production plant*

The reformer production plant considered in this study is a conventional reformer plant (natural gas used as feedstock) for the production of hydrogen. The production of enriched methane has been obtained adding the needed amount of methane to the hydrogen stream coming from the plant. A part of feedstock is used to produce electricity in a power station (installed power 100 MWe); in particular for 1 Nm^3 of enriched methane (17% of H_2) produced it has been considered a production of 0.58 kWhe. The technology installed refers to year 1988 (year of plant building) and has been considered as an average of 17 different reformer production plants installed in Europe.

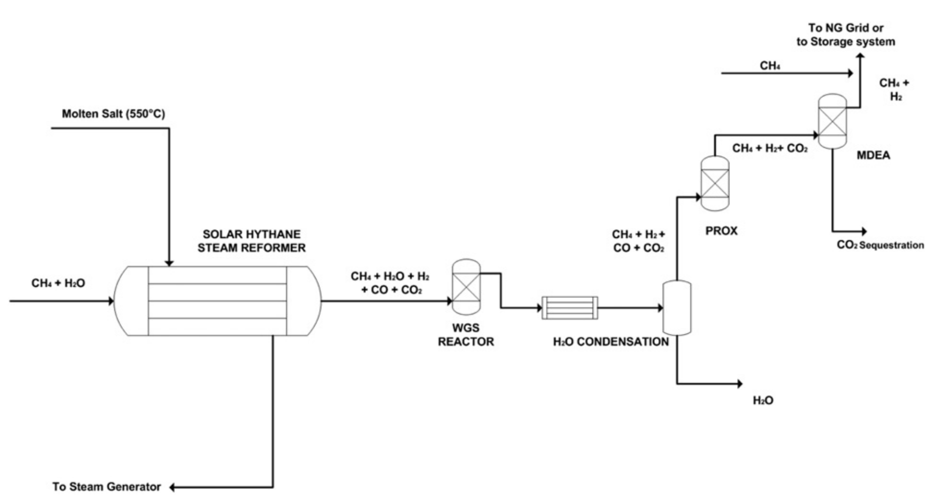

Fig. 1 – Solar enriched methane steam reforming layout.

3. Life cycle inventory (LCI) and LCA assessment methodology

3.1. *Life cycle inventory*

The LCI of the MS-CSP plant has been realized on the basis of aggregated data directly provided by the ENEA centre (data reported in Ref. [8]), while the LCI of the chemical plant (SR) has been realized on the basis of aggregated data provided by Tecnimont-KT (Italy).

The LCAs of the conventional cracker and reformer production plants have been performed by using data included in the Ecoinvent v.2.0 database [12]. Both for cracker and reformer plants we have used data referring to an average technology based on 17 production plant installed in Europe, with reference year 1988.

The data match well for the geographical position, while the reference years (2010 for MS-CSP-SR and 1988 for conventional production plants) can be considered a point of weaknesses of the LCIs used. In order to assess the LCI data reliability, it is also worth noting that all the data used in the LCAs are aggregated data (Table 1).

3.2. *LCA assessment methodology*

For the implementation of the system models the SimaPro7 LCA software has been used and the Eco-indicator 99 methodology, implementing a Damage Oriented Approach, has been chosen [13]. A detailed description of the method is also reported in Ref. [8].

Furthermore the Cumulative Energy Demand (CED) [12] method was also used to estimate the total energy requirements.

To maintain the study within a feasible scope, a limitation of detail (environmental burdens taken under consideration) in system modelling was necessary: the total cut-off was not to be more than 5% of input materials as referred to the functional unit.

4. Results and discussion

The most important LCA results for the MS-CSP-SR plant, in terms of single impact categories, are summarized in Table 2 and compared with the outputs of the other production plants assessed in this work. It is worth assessed that the relatively high values (in comparison to those found about the conventional product plants) shown for some impact categories (Human toxicity 100a, Acidification and Eutrophication) by the MS-CSP-SR power plant are mainly due to the environmental contribution of the building materials production. In effect, the solar technology is much less intensive than conventional technologies and requires a very high amount of stainless steel for the solar collector building etc. On the other hand, the production of stainless steel is characterized by a high impact on the environment, in particular for the Human Toxicity impact category.

Table 1 – Raw materials for the SR plant building for the whole plant life cycle (20 years) referred to the used functional units. Transport was implicitly included in energy consumption.

Raw material and electricity duty	Amount
Process & Cooling Water (kg)	0.065
Steel (kg)	1.41E-5
Stainless steel (kg)	2.43E-5
Mineral wool (kg)	7.12E-7
Molybdenum (kg)	2.93E-5
Nickel (kg)	2.51E-7
CH4 make-up (kg)	0.592
MDEA (kg)	8.01E-6
Electricity (Italian mix) (MJ/year) for auxiliary systems	0.092

Table 2 – Main LCA's results in terms of specific emissions of the functional unit obtained by the CML and CED methods [13].

Impact category	MS-CSP-SR	Cracker	Reformer
CED Non-renewable (MJ_{eq})	35.1	63.9	68.2
CED Renewable (MJ_{eq})	24.55	0.137	3.633
Global warming 100a ($kgCO_{2eq}$)	0.498	2.16	5.43
Ozone layer depletion 25a (kgCFC-11_{eq})	2.7E-08	2.17E-07	2.86E-07
Human toxicity 100a (kg1,4-DB_{eq})	0.154	0.435	0.115
Acidification ($kgSO_{2eq}$)	1.81E-2	1.43E-2	1.43E-2
Eutrophication ($kgPO_4^{3-}{}_{eq}$)	1.3E-3	8.2E-4	2.23E-3

The cumulative energy demand and mid-point impact categories LCAs results comparison among simulated plants are reported in Figs. 2 and 3.

From the pictures is clear that the MS-CSP-SR plant requires a high quantity of renewable energy (from solar, biomass, water), while fossil energy duty is about 50% less than that required from the conventional cracker and reformer production plants. These findings agree with a much lower emission in terms of $CO_{2,eq}$ (measured as Global Warming Potential) reported by the MS-CSP-SR plant with respect to these of the traditional production plants (see Table 2).

In Fig. 3 it is also reported the comparison of the three production plants by using the Eco-indicator 99 methodology in terms of impact categories (mid-point level). The aforementioned findings are confirmed: the MS-CSP-SR production plant leads to environmental advantages in terms of reduction of fossil fuels depletion and climate change effect. On the contrary, the wide use of molten salts and siliceous determines a relatively high impact of the MS-CSP-SR plant on the minerals depletion, as well as the high environmental impact for the categories “Ecotoxicity”, “Eutrophication/Acidification” and “Carcinogens” mainly due to the environmental burdens associated to the construction materials.

In order to draw wider and more general considerations on the LCA results, the mid-point level categories can be grouped in few damage categories following the criteria of the Eco-indicator 99 LCA method. Based on this methodology, the categories “Carcinogens”, “Respiratory organics”, “Respiratory inorganics”, “Climate change”, “Radiation” and “Ozone layer”

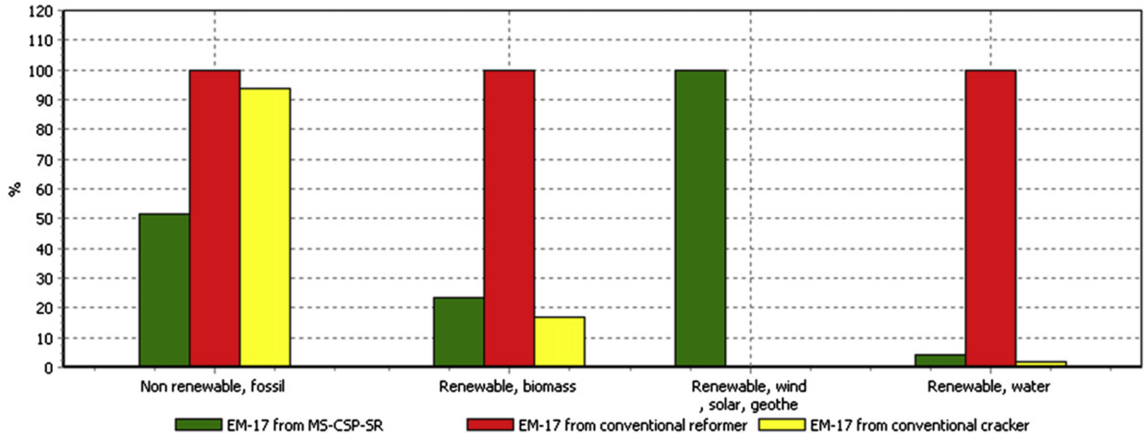

Fig. 2 – LCAs comparison in terms of Cumulative Energy Demand (CED).

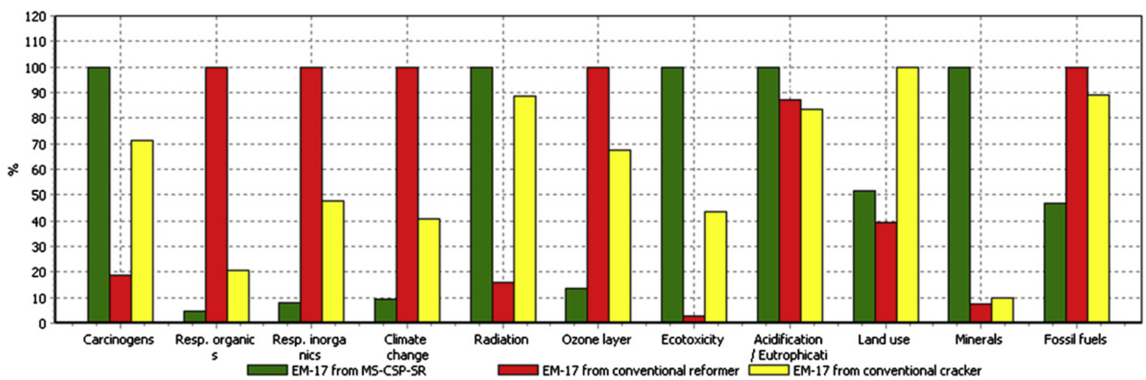

Fig. 3 – LCAs comparison in terms of mid-point impact categories (Eco-indicator 99).

are grouped in the damage category "Human Health", while the categories "Ecotoxicity", "Acidification/Eutrophication" and "Land use" flows in the damage category "Ecosystem quality". Finally, the categories "Minerals" and "Fossil fuels" are grouped in the damage category "Resources" which accounts for the depletion of non-renewable resources.

The LCA results in terms of damage categories are shown in Fig. 4, which clearly highlights the lower impact of the MS-CSP-SR plant both for the damage categories "Resources" and "Human Health", while its impact for the "Ecosystem Quality" is substantially comparable with these of the reformer and cracker production plants. Therefore, from an overall point of

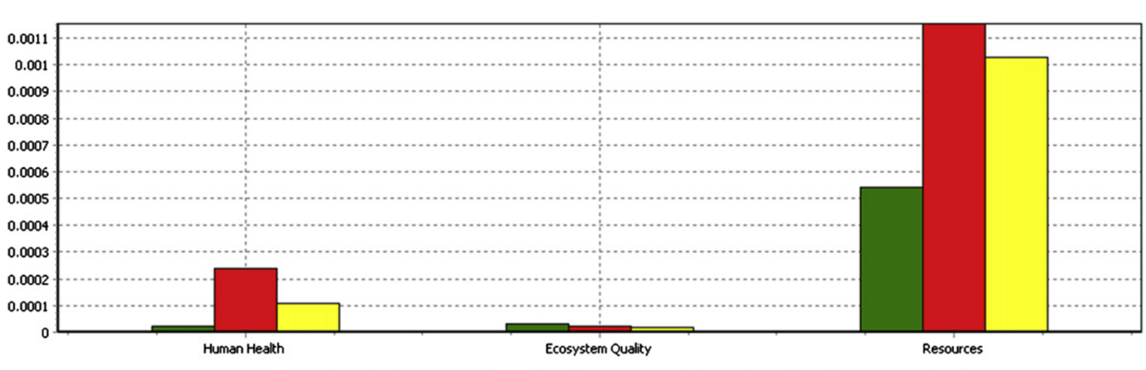

Fig. 4 – LCAs comparison by means of the Eco-indicator 99 methodology: damage oriented approach.

view, Fig. 4 suggests that the MS-CSP-SR plant is always preferable (in terms of environmental impact) to the reformer and cracker production plants.

5. Conclusions

In this work the performance of a MS-CSP-SR plant for the production of enriched methane was assessed from an environmental point of view by using the Eco-indicator 99 LCA methodology implemented in the Simapro7 LCA software. The MS-CSP-SR plant was compared to conventional production plants (cracker and reformer) in order to evaluate its reliability. The obtained results are much interesting: the MS-CSP-SR plant is preferable, from an environmental point of view, with respect to the conventional production plants. From one hand, this finding confirms the high potentials of this innovative plant technology, but it is also worth highlights that the MS-CSP-SR plant technology is a very young technology in comparison to the conventional production plants, therefore further developments must be still carried out.

To conclude, it is very important to draw some considerations about the reliability of LCA results reported in this study. Indeed, the LCA results are affected by the uncertainties associated with the choice of plants inventory data, or, form a more general point of view, by the data reliability reported in the Ecoinvent database. Furthermore, other uncertainties derive directly by the oriented damage approach: it is not so easy to translate the release of a chemical into how many years the human life will be reduced and what disabilities they will encounter; or to evaluate the damage to future generations caused by the depletion of non-renewable resources. Therefore, the LCA results reported in this work can be useful to draw first considerations about the environmental reliability of MS-CSP-SR plant.

List of Symbol

EM	Enriched Methane (EM)
ICEs	Internal Combustion Engines (ICEs)
CSP	Concentrating Solar Power plant
LCA	Life Cycle Assessment
MS-CSP-SR	Molten-Salt Concentrating Solar Power plant Steam Reforming reactor
WGS	Water–Gas Shift
PROX	Preferential Oxidation unit
MDEA	Methyldiethanolammine
LCI	Life Cycle Inventory
CED	Cumulative Energy Demand
CFC-11	Chloro Fluoro Carbures-11
1,4-DB	1,4-Dichlorobenzene

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